



Contents lists available at ScienceDirect

Ain Shams Engineering Journal

journal homepage: www.sciencedirect.com

Civil Engineering

Effect of metakaolin replaced granulated blast furnace slag on fresh and early strength properties of geopolymer mortar

Ghasan F. Huseien^{a,*}, Jahangir Mirza^{a,b}, Mohammad Ismail^a, S.K. Ghoshal^c, Mohd Azreen Mohd Ariffin^a^a Department of Structure and Materials, Faculty of Civil Engineering, Universiti Teknologi Malaysia, 81310 UTM Johor Bahru, Johor, Malaysia^b Department of Materials Science, Research Institute of Hydro-Quebec, 1800 Mte Ste. Julie, Varennes, Quebec J3X 1S1, Canada^c Department of Physics, AOMRG, Faculty of Science, Universiti Teknologi Malaysia, 81310 UTM Johor Bahru, Johor, Malaysia

ARTICLE INFO

Article history:

Received 10 August 2016

Revised 15 November 2016

Accepted 17 November 2016

Available online xxxx

Keywords:

Geopolymer

Metakaolin

SiO₂:Na₂O

Compressive strength

Bond strength

ABSTRACT

We report the effect of metakaolin (MK) substituted granulated blast furnace slag (GBFS) on the early strength of geopolymer mortars (GPMs) for potential repair applications. Such GPMs were prepared by activating MK (0–15%) replaced GBFS. Solution concentrations ratio of SiO₂:Na₂O were varied in the range of 1.08–1.26 to achieve appropriate geopolymerization. Various proportion of Na₂O:dry binder (7, 8, 9, 11 and 13%) were used. The mass ratios of sodium silicate to sodium hydroxide (NS:NH) and the binder to fine aggregate (B:A) were fixed to 3.0 and 0.90, respectively. The mechanical properties of the synthesized GPMs were determined at ambient temperature after 24 h of casting and curing. It is demonstrated that 5% of MK replaced GBFS with 1.16 of SiO₂:Na₂O and 0.40 of S:B achieved an early compressive strength as much as 47.84 MPa at 24 h. The bond strength results exhibited the prospect of such GPMs as suitable alternative repair material.

Production and hosting by Elsevier B.V. on behalf of Ain Shams University. This is an open access article under the CC BY-NC-ND license (<http://creativecommons.org/licenses/by-nc-nd/4.0/>).

1. Introduction

Repair or rehabilitation is the major concern regarding several deteriorated concrete structures around us [1–4]. Such repairs of concrete structures are necessary to assure their service lifetimes. Moreover, they must be completed in a short time for public convenience [3,5]. Over the years, several repair materials are developed for concrete structures including cement-based materials, polymers, latex, etc. [5,6]. Lately, GPMs revealed tremendous prospects towards emergency repairs and coating [7–11]. The notion of GP was first introduced in the late 1970s, where aluminosilicate binders was activated by alkali solution to describe a family of GP [12]. The formation of GP was based on the reaction between the two parts of materials such as the alkali activator and the reactive aluminosilicate precursor (mainly MK) [13]. The GP based on alkali activation of MK became attractive not only because of its excellent thermal stability (better than conventional polymer material) but also due to its comparable mechanical properties to cement. Presently, GPMs are considered as a green alternative to Portland cement [14].

Despite the wide usage of fly ash (FA) and slag as two major materials in commercial GP products, MK emerged as most promising future feedstock materials for GP. It is needless to mention that MK possesses more consistent chemical compositions than FA and slag. Thus, it results in more reliable and predictable products that are suitable for repairable construction materials. Actually, both FA and slag are not abundant in many countries because of their effective usage in the manufacture of blending cements and concrete [15,16]. On top, the cost and technical challenges of supply chain limits their widespread usage [17]. Thus, the use of MK (together with other Al- and Si-bearing minerals) as raw materials appears more prospective and practicable [13].

Recently, intensive researchers are carried out on GPMs to understand the mechanism of geopolymerization and optimization of the product for achieving improved strength. Bernal et al. [18] studied the evolution of the binder structure of sodium silicate-activated slag-MK blends, where the effect of MK addition on the final strength of the binder is examined. Silva and Sagoe-Crenstil [19] determined the effect of different ratios of Al₂O₃ and SiO₂ on the setting and the hardening of the GP system. It is acknowledged that this ratio indeed affects the setting time and the final strength of the achieved GP. Chindaprasirt et al. [20] investigated the influence of SiO₂:Al₂O₃ on the setting time, the workability, and the final strength of the GP system and found the best ratio for GP binder (SiO₂/Al₂O₃) around 2.87–4.79.

Peer review under responsibility of Ain Shams University.

* Corresponding author.

E-mail address: eng.gassan@yahoo.com (G.F. Huseien).<http://dx.doi.org/10.1016/j.asej.2016.11.011>

2090-4479/Production and hosting by Elsevier B.V. on behalf of Ain Shams University.

This is an open access article under the CC BY-NC-ND license (<http://creativecommons.org/licenses/by-nc-nd/4.0/>).

Please cite this article in press as: Huseien GF et al. Effect of metakaolin replaced granulated blast furnace slag on fresh and early strength properties of geopolymer mortar. Ain Shams Eng J (2016), <http://dx.doi.org/10.1016/j.asej.2016.11.011>

In the past few years, several researchers [21–25] have attempted to utilize GP as a repair material by testing their slant shear, pull-out, and direct shear. Hu et al. [21] studied the bond strength between mortar substrate and GP in sandwich specimens. Geopolymer exhibited higher bonding strength than that of comparable Portland cement mixture. Pacheco-Torgal et al. [22] determined the bond strength between concrete substrate and GPM that were produced from tungsten mine waste containing calcium hydroxide. Phoo-ngernkham et al. [23,24] examined the effect of molarity of sodium hydroxide, sodium silicate content and calcium to silicate ratio on shear bond of geopolymer mortar as repair material. They found that geopolymeric binders possess very high bond strength even at an early age as compared to commercial repair products.

Considering these interesting attributes of MK, we inspected the effect of MK on the early bond strength of GPM to realize its potential as repair material. The so called bond strength between a repair material and an existing concrete being one of the most critical factors impacting the repair durability was evaluated using a splitting tensile and slant shear test of the produced GPMs. Tests were systematically conducted to characterize the bond strength between fabricated GPMs and mortar substrate. The results were analyzed, discussed and compared with commercially available repair materials.

2. Experimental protocol

2.1. Raw materials characterization

2.1.1. Metakaolin

Metakaolin (MK) is mainly characterized as a source of aluminosilicate for the preparation of GP. In this study, we followed the earlier procedures to prepare MK from kaolin through a dihydroxylation in the furnace, where kaolin was calcined at 750 °C for 6 h [26]. Kaolin powder (grade KM40) was purchased from the kaolin Malaysia SDN (Puchong, Selangor).

MK have distinctive whitish colour close to that of the parent kaolin material. Moreover, the appearance of kaolin has changed from pure white to floral whitish after dehydroxylation process. Malvern mastersizer micro particle size analyzer was used to determine the particle size distribution of MK. Fig. 1 illustrates the result of particle size analysis. The particle of MK cut at 1 µm was found to be characteristically below 100 µm, where 75% of MK had passed through 10 µm. The FESEM images of MK sample revealed irregular platy. Angular shaped particles were observed

to be closely packed in lumps with disorder arrangements as depicted in Fig. 2. The tiny lumps observable in their physical form may be noticed in the micrograph appearing as stacks of layers of MK sheets. The X-ray diffraction (XRD) patterns of MK (Fig. 3) showed a broad hunch between 9.8° and 28° and a sharp crystalline peak at 26.8°, which are allocated to the presence of amorphous structure of quartz (SiO₂), mullite (Al₆Si₂O₁₃), Andalusite (Al₂SiO₃), Calcium Oxide (CaO), Magnesium silicate (MgSiO₂) and Aluminum Magnesium (AlMg) crystalline phases. The quartz is generally known to be unreactive while the presence of Muscovite (KAl₂(Si₃Al)O₁₀(OH.F)₁₂) which is impurity from the client is consumed during synthesis [26].

The chemical compositions of MK were determined using X-ray Fluorescence Spectroscopy (XRF). The XRF results revealed that the major constituents of MK are silicon oxide (SiO₂) and alumina oxide (Al₂O₃). Other components include ferric oxide (Fe₂O₃), calcium oxide, magnesium oxide, potassium oxide, etc. The typical chemical composition of MK is depicted in Table 1. Metakaolin should meet the requirements of ASTM C618 [27] (SiO₂ plus Al₂O₃ and Fe₂O₃) more than 85%.

2.1.2. Ground blast furnace slag

The cement-free binder is made using GBFS as one of the resource materials, which is collected from Ipoh (Malaysia). GBFS possesses both cementitious and pozzolanic properties and is considered to be different from other supplementary cementitious materials. GBFS develops its own hydraulic reaction when mixed with water and is off-white in colour. The result of particle size showed that more than 60% particle has size lower than 10 µm (Fig. 1). Fig. 2 displays the FESEM images of GBFS, which consisted of irregular, angular as well as spherical particles with a smooth surface (Fig. 2b). The XRD pattern (Fig. 3) of as-received GBFS revealed mainly the amorphous phase with a small amount of magnetite. The GBFS comprising of calcium silicate and alumina (about 90%) meets the requirement of pozzolanic material [27]. Table 1 summarizes the chemical composition of GBFS.

2.1.3. Alkali solution

The alkaline solution used in the present study was a mixture of sodium silicate (NS) and sodium hydroxide (NH, purity 98%). These were used to activate the alumina and silica in MK and GBFS. The NS solution was composed of SiO₂ (29.5 mass%), Na₂O (14.70 mass %) and H₂O (55.80 mass%). These chemicals were purchased from QREC (ASIA) SDN BHD (Malaysia). A different amount of pellets was dissolved in water to prepare NH solution of various molar concentrations (10, 14, 16 and 18 M). The solution was left for 24 h to be cool, then it was added to a NS solution to prepare the final alkaline solution with different mass ratios of SiO₂:Na₂O as enlisted in Table 2. The ratio of NS to NH was fixed for all mixtures.

2.1.4. Fine aggregate

Naturally occurring siliceous river sand was used to make all mortar specimens. The sand was dried in the oven at 60 °C for 24 h for controlling the moisture content. The sand was graded to conform to ASTM C33 [28] standard specification as depicted in Fig. 4. Fineness modulus of the aggregate and specific gravity were discerned to be 2.9 and 2.6, respectively.

2.1.5. Super plasticizer

To increase the workability of GPM, super plasticizer type (Sika Visco Crete-3430) was used. The utilization of viscosity modifying admixture (VMA) provides more possibilities of controlling segregation (stability) and homogeneity of the mix. The amount of SP was kept fixed for all mixtures with 3% of the binder.

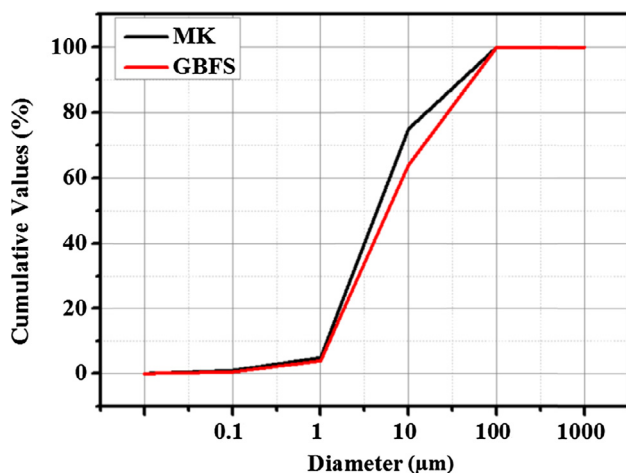


Figure 1. Cumulative particle size distribution of MK and GBFS.

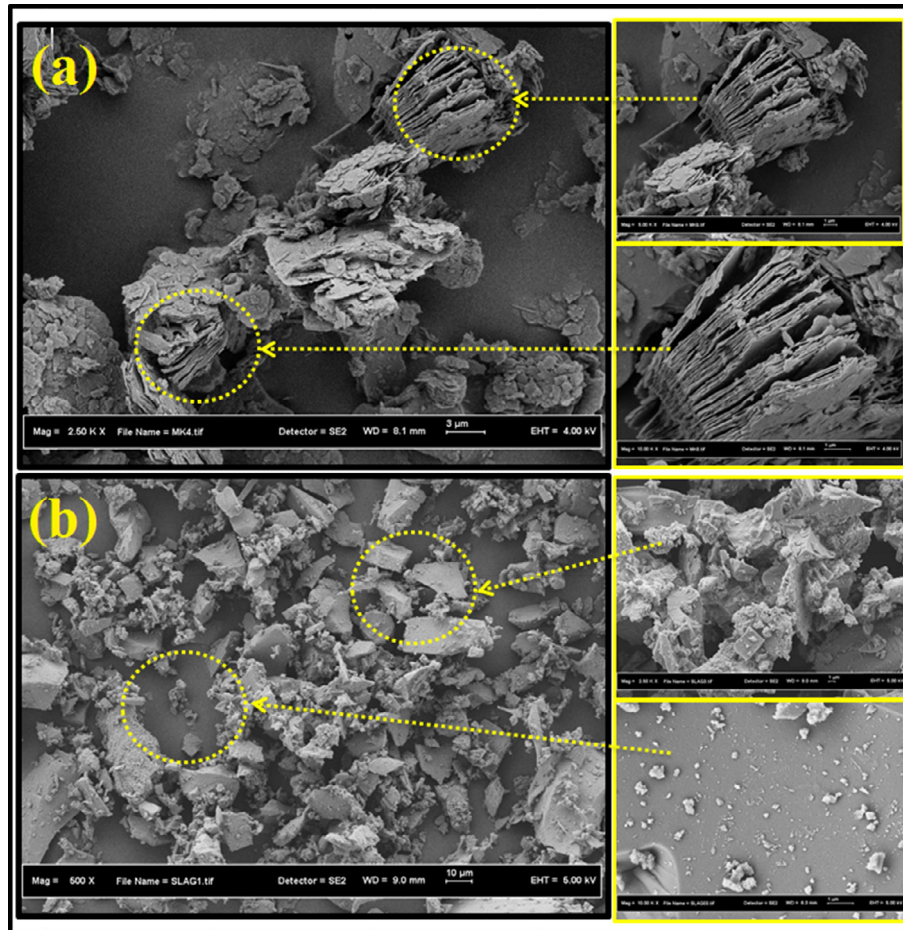


Figure 2. FESEM images of (a) MK, and (b) GBFS.

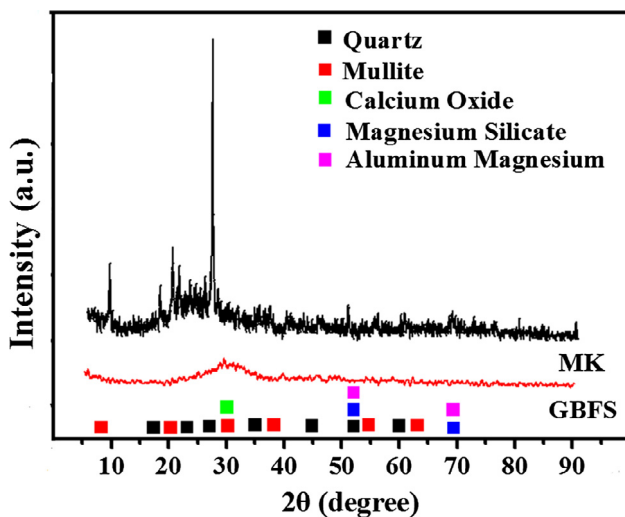


Figure 3. XRD patterns of MK and GBFS.

2.1.6. Ordinary Portland cement

The ordinary Portland cement is obtained from Holcim Cement Manufacturing Company (Malaysia) conforming to ASTM C150 standard specification for Portland cement of 2009. This was used to prepare cement mortar samples. The calcium oxide (CaO) content was found to be around 62.7 mass%. CaO is considered to be the important composition of OPC as far as the hydration process is concerned. Actually, the CaO content in OPC must be very high.

2.2. Mix proportion and curing condition

Fig. 5 displays the four stages of mix proportions of GPMs. First, the effect of MK replacement by an amount of 0, 5, 10 and 15 mass% on GBFS was inspected, where other parameters were kept constant for all mixtures to select the optimum ratio of MK substituted GBFS (Table 3). The high early strength after 24 h is the criteria to select the optimum mixture at all stages. Second, the impact of varying alkaline solution concentration ratio ($\text{SiO}_2:\text{Na}_2\text{O}$) of 1.26, 1.16, 1.12 and 1.08 on the strength of prepared mortars (optimum MK replaced GBFS from stage 1) was examined, where the alkaline solution to binder ratio (S:B) constant (0.65) for all mixtures were

Table 1
Chemical compositions of GBFS and MK (mass%).

Materials	SiO ₂	Al ₂ O ₃	CaO	MgO	Fe ₂ O ₃	Na ₂ O	K ₂ O	TiO ₂	MnO	P ₂ O ₅	LOI
MK	52.22	41.41	0.08	0.26	0.49	0.01	1.73	0.01	0.01	0.13	1.66
GBFS	30.53	13.67	46.02	5.09	0.33	0.24	0.36	–	–	0.01	0.22

Table 2
Compositions of alkaline solution.

Alkaline Solution	NaOH solution (NH)			Na ₂ SiO ₃ solution (NS)			NS:NH mass%	SiO ₂ :Na ₂ O mass%
	Molarity M	Na ₂ O mass%	H ₂ O mass%	SiO ₂ mass%	Na ₂ O mass%	H ₂ O mass%		
S1	10	28.5	71.5	29.5	14.7	55.8	3.0	1.26
S2	14	35.9	64.1	29.5	14.7	55.8	3.0	1.16
S3	16	39.2	60.8	29.5	14.7	55.8	3.0	1.12
S4	18	42.1	57.9	29.5	14.7	55.8	3.0	1.08

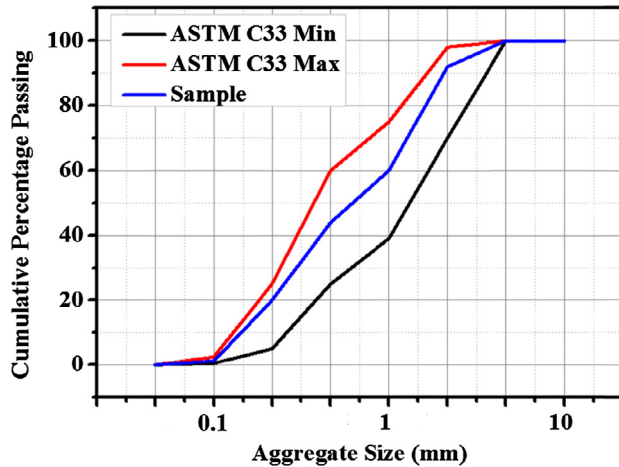


Figure 4. Particle size analysis of fine aggregate.

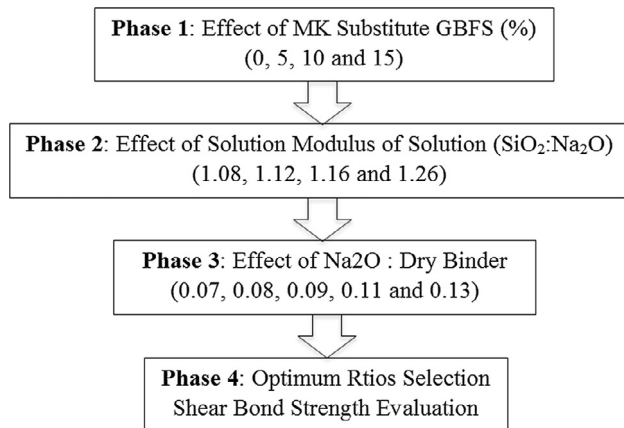


Figure 5. Mixtures procedures.

kept constant. Third, the effect of various (7, 8, 9, 11 and 13%) Na₂O:dry binder on the strength of prepared mortars (the optimum percentage of MK substituted GBFS and the optimum alkaline solution obtained from phase 1 and 2, respectively) was determined. The NS to NH ratio of 3.0, binder to fine aggregate ratio (B:A) of 0.90 and amount of super-plasticizer (SP of 3%) were kept constant in all three stages (Table 3) for the mixtures 1, 2 and 3. In the fourth stage, the optimum ratios from the previous three stages are selected to evaluate the bond strength of GPM. The results are compared with normal OPC mortar as a control sample (NC).

The control sample was made of ordinary Portland cement, fine aggregates and water. Fine aggregate to cement ratio by mass of 3:1 was considered. The fine aggregate was kept in a saturated surface under dry condition. The water to cement (w:c) ratio was set at 0.48.

Present GPMs were prepared by mixing MK with GBFS over a period of 4 min at dry condition to achieve a homogenous mixture of fine aggregates. Then, the acquired mixture was activated by adding the alkaline solution to obtain a thorough mixed mortar cast into 50 mm cube moulds. The flow of the fresh GPM was measured to examine the effect of different parameters on the workability and setting time. The casting was performed in two layers, where each layer was compacted with vibration table for 15 s. The samples were left for 24 h after casting and before opening the moulds as well as curing at ambient temperature (27 °C and 75% Relative Humidity). They were tested for 1, 3, 7 and 28 days to evaluate the compressive strength (according to ASTM 109 [29]) and other mechanical properties. Table 3 depicts the achieved three different phases of mixtures.

2.3. Testing methods

2.3.1. Fresh properties of GPMs

Flow ability of geopolymer mortar was measured using a flow table method modified from ASTM C230, "Standard Specification for Flow Table for Use in Tests of Hydraulic Cement". The flow table provides an efficient means of determining the flow of cement pastes and hydraulic cement mortars. Vicat needle was used to

Table 3
Mix proportions of GPMs.

Phase	Binder mass%		Alkaline solution type ^a	S:B mass%	SP mass%	B:A mass%	Na ₂ O:dry binder mass%	H ₂ O:dry binder mass%
	GBFS	MK						
1	100	0	S3	0.65	0.03	0.9	0.135	0.37
	95	5						
	90	10						
	85	15						
2	95	5	S4	0.65	0.03	0.9	0.14	0.37
			S2				0.13	0.38
			S1				0.12	0.39
			S2				0.11	0.32
3	95	5		0.55	0.03	0.9	0.09	0.26
							0.08	0.23
							0.07	0.20

^a From Table 2.

measure the setting time (according to ASTM C191 standard), where the specimen was placed on the Vicat apparatus to measure the initial and final setting time.

2.3.2. Mechanical properties of GPMs

Cubic moulds of size 50 mm, cylinder of dimension (75 mm × 150 mm) and prism of dimension (40 mm × 40 mm × 160 mm) were used to prepare compressive, tensile and flexural strength samples. Compressive, tensile and flexural strengths of GPMs were measured using ASTM C109/109M standard [29]; ASTM C496/C496M-11 [30] and ASTM C78 [31], respectively. The strengths were evaluated and compared with the control sample (cement mortar). The samples compressive strength was evaluated at the age of 1, 7, and 28 days. Three samples averaging are performed to present the results.

2.3.3. Shear bond strength between NC and GPM

ASTM C882 [32] was depended to evaluate the shear bond strength capacity between the Portland cement substrate (NC) and GPM with stiffer slant shear angle 30°. For casting of the specimens, the NC was casted and cured for 3 days in the water. Afterward, these specimens were left in the lab (27 °C and 75% Relative Humidity) till they were reached at the age of 28 days. Next, they are fixed in cylinder moulds (100 mm × 200 mm), casted for the second part (OPC and GPM) and then evaluated after 1, 3, 7 and 28 days. The shear bond strength was defined as the ratio of maximum load at failure and the bond area. The reported results of shear bond strength were considered as the average of three samples. The procedure of shear bond test was presented in Fig. 6.

3. Results and discussion

3.1. Fresh properties of GPMs

Two different tests such as flow and setting time were performed on fresh state mortar. Figs. 7 and 8 illustrate the effect of MK replaced GBFS on the flow and the setting time of GPMs, respectively. The flow of the mortar was found to increase with increasing percentage of MK replaced GBFS, which was attributed to the differences in the physical properties and chemical reactions of the mixtures. Furthermore, with the reduction of the GBFS content, the number of angular particles was reduced and helped to improve the flow ability of the mortar mixture. Also the calcium

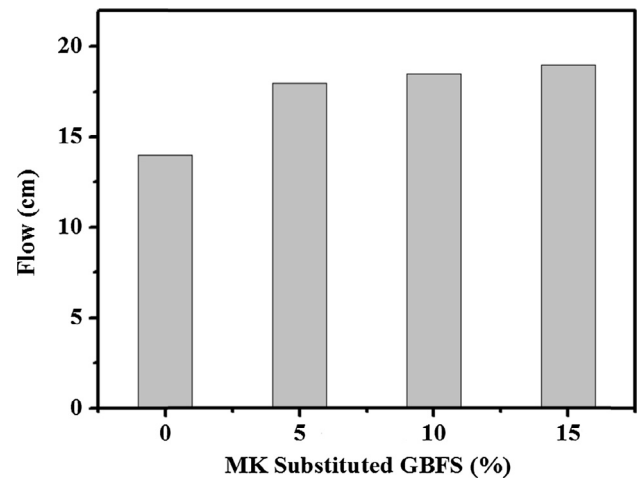


Figure 7. Impact of metakaolin (MK) substituted GBFS on flow of GPMs.

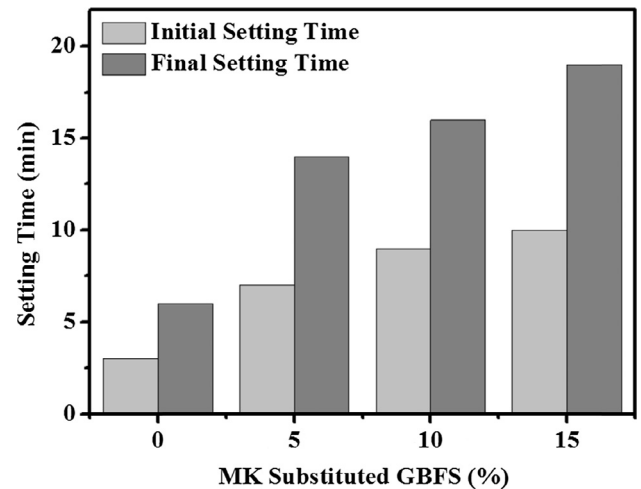


Figure 8. Impact of metakaolin (MK) substituted GBFS on setting time of GPMs.

content was decreased with increasing MK content. Furthermore, the silicate and aluminum content was increased. More silicate content was useful for improving the flow ability of the mortar.

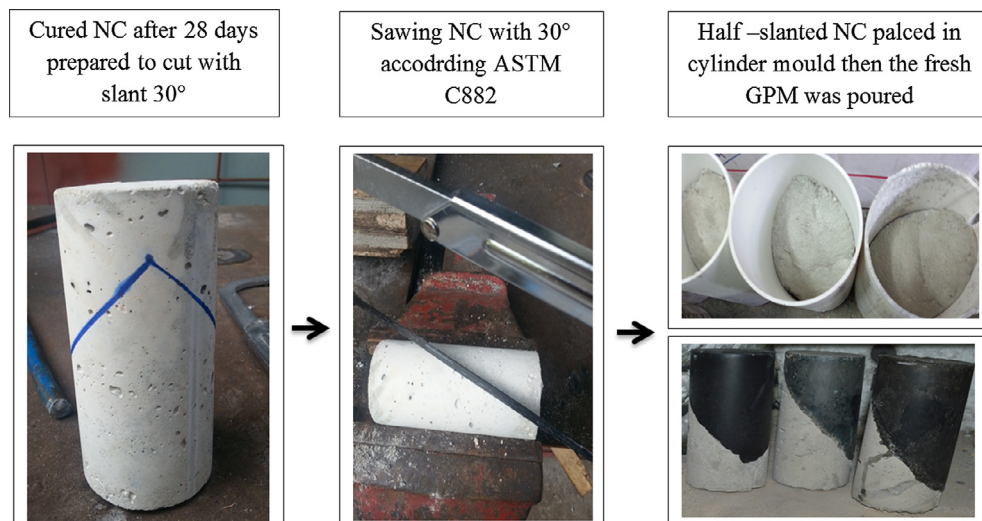


Figure 6. Bond strength method.

The fineness in the particle size of MK (75% of them less than 10 μm) has also contributed towards the increase of workability of the mortar. Similar trends were also reported earlier [33], where the particle size played an important role and affect the dissolution and flow of the mortar. On top, admixing of MK and GBFS produced a slow setting and enhanced the workability as shown in Fig. 7. This observation is supported by the findings of al Al-Majidi et al. [34].

Fig. 8 demonstrates the effect of MK replaced GBFS on the setting time of GPM. It was observed that a decrease in the calcium content led to an enhancement in the initial and final setting times as reported elsewhere [23,33,35]. Furthermore, an increase in the MK content has enhanced the SiO_2 and Al_2O_3 concentrations, thereby improved the setting time [20]. The rate of setting was increased significantly as indicated by the substantial difference in the initial setting time. The difference between initial and final setting time was also increased with the reduction of GBFS content in the mortar. This finding is also supported the fact that higher the GBFS content in the mortar, the quicker is the rate of setting [36,37]. Thus, it is established that MK as a part of the binary blended binder is greatly effective to decelerate the setting time of GPMs under ambient condition.

Fig. 9 shows the effects of alkaline solution molarity variation on the flow of GPMs. The flow of the mortar was found to be higher at lower Na_2O content. The flow of GPMs was reduced from 23 to 15 cm as the Na_2O amount was enhanced with NaOH molarity increase from 10 to 18 M. Fig. 9 displays the solution molarity dependent variation on the workability of GPMs. An increase in the Na_2O content was observed to diminish the flow. Besides, an increase in the Na_2O content in the alkaline solution led to an increase in the sodium ion (Na^+) content and reduced the (SiO_2 : Na_2O) ratio as depicted in Table 2. This led to an increase in the heat released, thereby affected negatively the flow ability and setting time [18,38,39].

Fig. 10 depicts the influence of Na_2O content on the setting time of GPMs. The GPMs activated at low NaOH molarity took significantly longer time to set. This is due to slow rate of chemical reaction at low ambient temperature and little amount content of Na_2O . In this study, the GPM mixtures that were prepared with high concentration of solution revealed very fast setting time. The GPMs setting time was further improved considerably with the reduction of NH molarity. Both initial and final setting time was enhanced with the decrease of NH molarity. Besides, the rate of setting was increased appreciably as indicated by the substantial difference in the initial setting time. The difference between initial

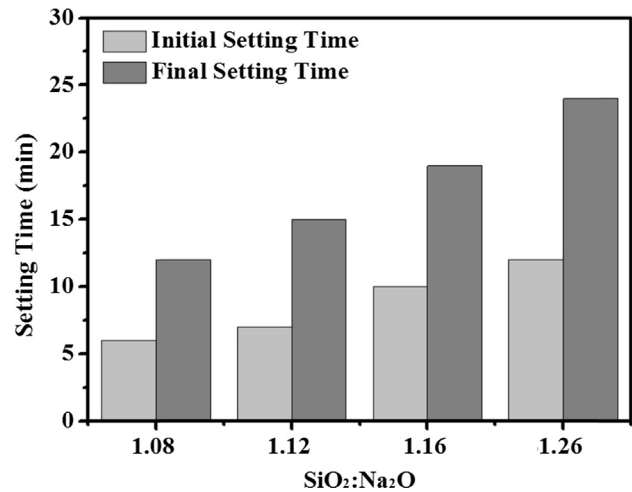


Figure 10. Impact of SiO_2 : Na_2O on the setting time of GPMs.

and final setting time was also increased with the reduction of NH molarity in the mortar. This enhancement of setting time at lower NH molarity was attributed to the slower rate of setting [38].

Fig. 11 presents the effect of S:B on the flow of GPMs. The flow ability of mortar was increased with increasing S:B. An increase in the solution has increased the water content (H_2O :dry binder) and improved the workability (Table 3). Fig. 12 represents the influence of solution content on the setting time of GPMs. As mentioned earlier, the GPM activated at high solution content was set at longer time because of the slow rate of chemical reaction. The GPMs setting time was improved considerably with the increase of solution content. Both initial and final setting time was enhanced also with the increase of S:B.

3.2. Effect metakaolin on mortar density

Fig. 13 illustrates the effect of MK substituted GBFS on the density of GPMs. The density of GPMs was found to increase with increasing percentage of MK replacement. The particle size and specific gravity of MK was found to influence the GPMs density. An increase in the content of Al_2O_3 and SiO_2 led to produce sodium aluminosilicate hydrate (NASH) gel beside the calcium silicate hydrate (CSH) which in turn improved the microstructure of GPMs as evidenced earlier [25].

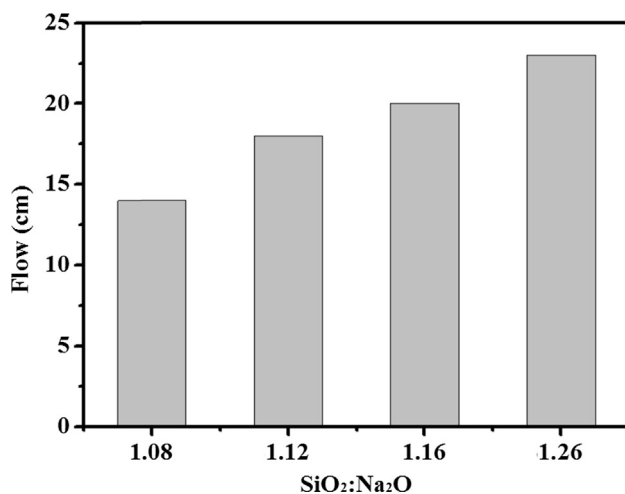


Figure 9. Impact of SiO_2 : Na_2O on the flow of GPMs.

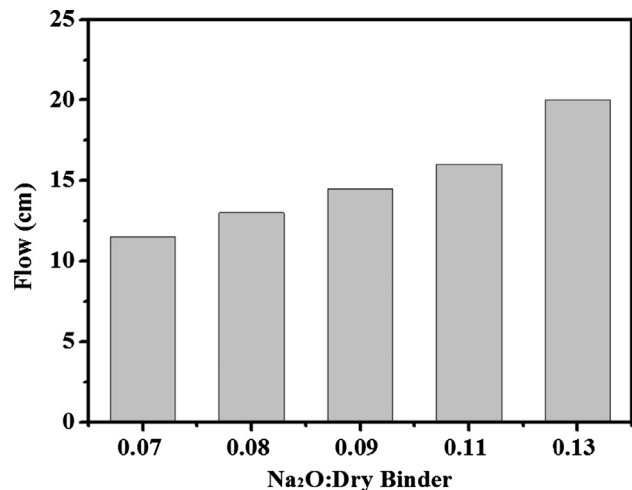


Figure 11. Impact of varying Na_2O :dry binder on flow of GPMs.

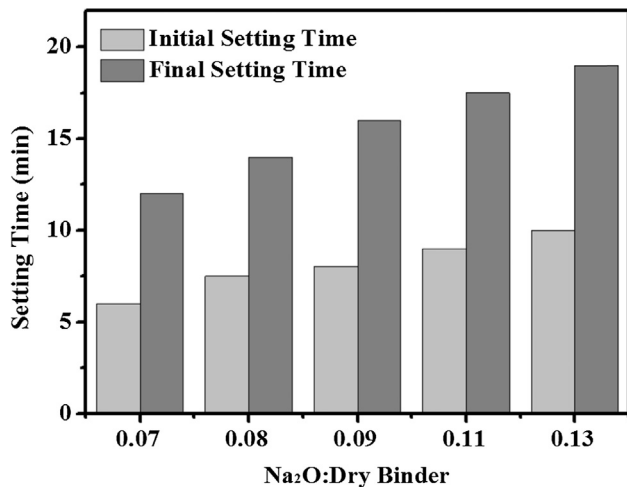


Figure 12. Impact of varying Na₂O:dry binder on the setting time of GPMs.

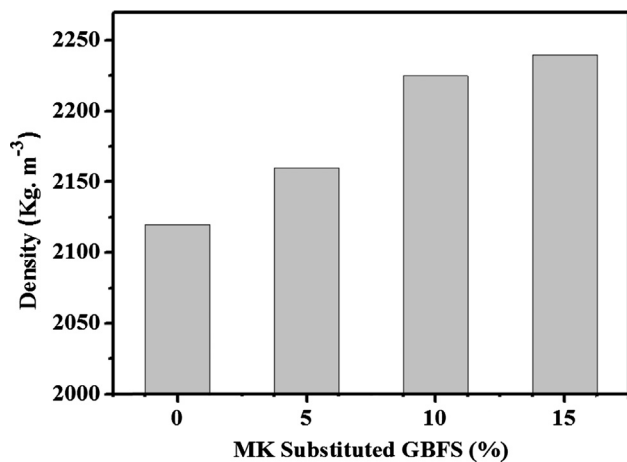


Figure 13. Effect MK substituted GBFS on GPMs density.

3.3. Compressive strength

Effect of MK replaced GBFS, modulus of solution (SiO₂:Na₂O) and (Na₂O:dry binder) on the early compressive strength of GPMs were determined. Compressive strength of GPMs was measured after 1, 7 and 28 days using ASTM C109/C109M and averaged over three realizations.

3.3.1. Effect MK replaced GBFS

Fig. 14 shows the impact of MK substitution on the early compressive strength of GPMs. The compressive strength of MK replaced GBFS sample after 1 day revealed lower values (27.6, 24.2 and 20.4 MPa) with 5, 10 and 15% respectively, than the one prepared without MK (32.8 MPa). However, after 28 days the MK substituted samples (5, 10 and 15 mass%) achieved higher strength (62.5, 62.8 and 63.1 MPa) than the one prepared without MK (44.8 MPa). This observation was majorly ascribed to the increase in curing time and the completion of geopolymerization process. Increase in the content of Al₂O₃ and SiO₂ has improved the geopolymerization and produced sodium aluminosilicate hydrate (NASH) and CASH gel in addition to the calcium silicate hydrate (CSH), thus enhanced the strength properties of GPMs [25,40]. GPM mixture with 5% MK replaced GBFS showed a high early compressive strength compared with the other percentages, which was selected for the second stage.

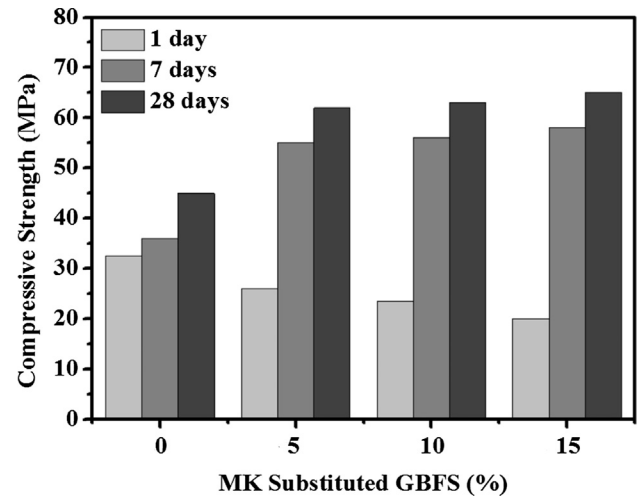


Figure 14. Impact MK substituted GBFS on the early compressive strength of GPMs.

3.3.2. Effect solution modulus (SiO₂:Na₂O)

Fig. 15 displays the influence of varying NaOH molarity on the development of compressive strength. The effect of sodium hydroxide solution molarity on SiO₂ to Na₂O ratios when added with sodium silicate solution, the ratio of NS:NH and the direct effect of NH molarity on SiO₂:Na₂O ratio are determined. An increase in the NH molarity has enhanced the Na₂O contents and reduced the silicate to sodium ratio as enlisted in Table 2. The compressive strength was increased with the SiO₂:Na₂O ratio. Consequently, the compressive strength was related to the amount of NaOH in the alkaline solution. As the SiO₂ to Na₂O ratio was increased the degree of dissolution and hydrolysis were accelerated, thereby inhibited the polycondensation. A solution molarity of 14 M (SiO₂:Na₂O of 1.16) showed high early strength compared to other molarities. Zuhua et al. [41] reported that the presence of high concentration of NH has accelerated the dissolution of silica and alumina and thus hindered the polycondensation. Samples prepared with 18 M of NH (low SiO₂:Na₂O of 1.08) displayed lower strength than those prepared with 10, 14 and 16 M [39]. Phoo-ngernkham et al. [24] reported the dissolution of calcium was suppressed at high NaOH concentration resulting in less hydration products. In addition, An excess hydroxide ion caused aluminosilicate gel precipitation at the early stage and resulted in lower strength geopolymers [42]. GPM mixture prepared with 14 M

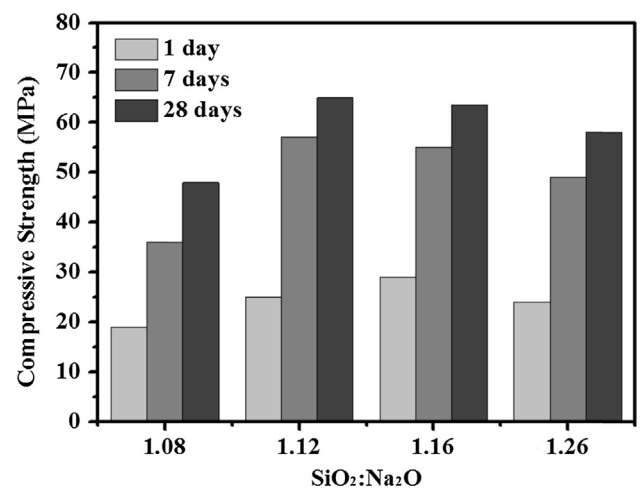


Figure 15. Impact of SiO₂:Na₂O on the early compressive strength of GPMs.

($\text{SiO}_2 : \text{Na}_2\text{O} = 1.16$) revealed the higher early strength after 24 h and thus selected for the next stage.

3.3.3. Effect Na_2O :dry binder

Fig. 16 depicts the effect Na_2O :dry binder on the development of compressive strength. An increase in the solution to binder (S:B) content lead to an increase in the ratio of Na_2O :dry binder and H_2O to dry binder as summarized in Table 3. A reduction in the S:B was found to increase the early strength of GPMs. Samples prepared with 8% of Na_2O :dry binder and 23% of H_2O :dry binder exhibited the highest early strength of 47 MPa/24 h and 63 MPa/28 days, respectively compared to other ratios. In other words, the presence of too much water reduced the geopolymerization rate as reported by Zuhua et al. [41]. Huseien et al. [25] reported that an increase in the alkaline solution to binder could increase the water content and reduce the amount of CASH and NASH gel. Consequently, a poor structure could be produced with low early strength.

3.4. Splitting tensile strength

Fig. 17 compares the splitting tensile strength of prepared GPMs with OPC mortar. Twelve cylindrical samples were prepared using the optimum results from phase 3, where 5 wt.% of MK replaced GBFS, 14 M of NH ($\text{SiO}_2 : \text{Na}_2\text{O} = 1.16$) and 8% of Na_2O :dry binder were used. The tensile strength of all samples cured at ambient temperature revealed an increase with increasing curing time. Moreover, all the samples demonstrated higher early split tensile strength compared with control samples (OPC). After 24 h, the GPM exhibited a split tensile strength of 2.95 MPa which was almost 10 times greater than that of OPC mortar (0.32 MPa). The ability of using GPM as a new alternative repair material was clearly depicted in the results of tensile strength. Similar trends were reported elsewhere [23].

3.5. Flexural strength

Fig. 18 presents the flexural strength of GPM prisms. Flexural strength were evaluated after 1, 3, 7 and 28 days and compared with OPC (as control samples). After 24 h, GPM achieved a very high early flexural strength (5.7 MPa) in comparison to the control samples (OPC) which was as low as 0.6 MPa. The early flexural strength of GPM was further increased to 8.2 MPa after 28 days. The geopolymerization has contributed more SiO_2 and Al_2O_3 to the dissolution and produced the NASH and CASH gel beside the

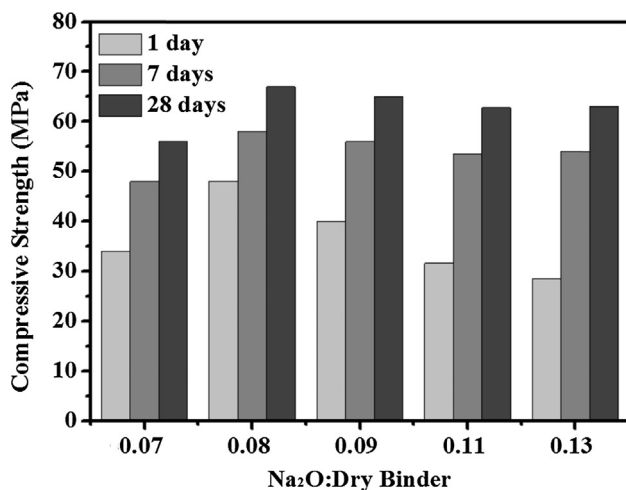


Figure 16. Impact of Na_2O :dry binder on the early compressive strength of GPMs.

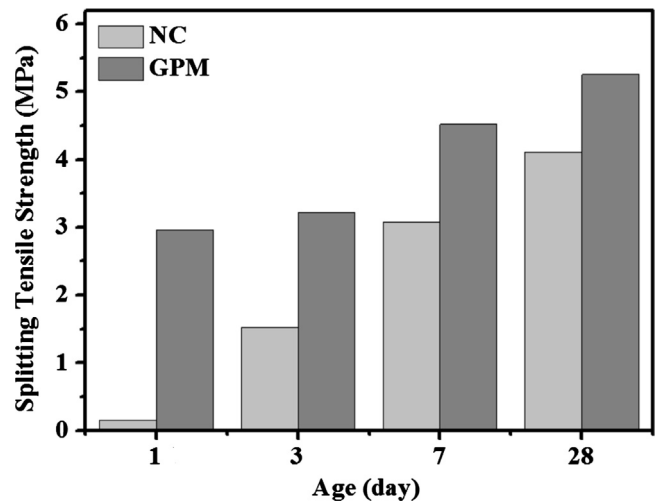


Figure 17. Curing time dependent development of early split tensile strength of GPMs as compared to OPC mortar.

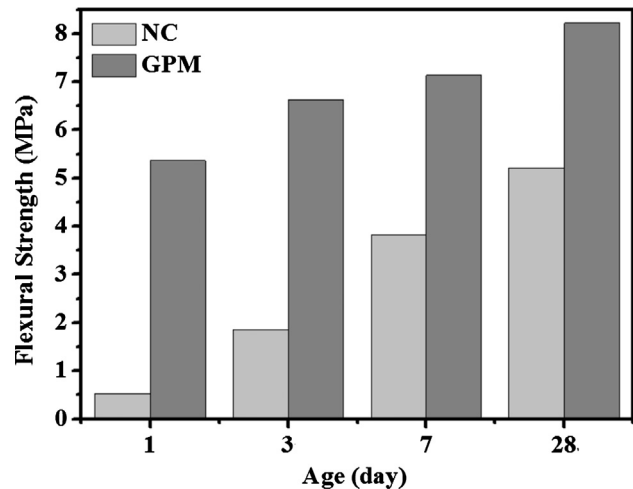


Figure 18. Flexural strength of GPMs as compared to OPC mortar.

CSH gel. This explains the occurrence of higher strength of GPM compared to OPC sample which depended only on the calcium silicate hydrate (CSH).

3.6. Bond strength

The bond strength between OPC (NC) and GPM was determined using a slant shear bond test. Cylinder slant shear specimens of dimension (100 mm × 200 mm) with interface line at 30° (Fig. 9) are prepared. The bond strength was tested at 1, 3, 7 and 28 days after curing at ambient temperature. The slant shear test is the most widely accepted test for the bonding of repair materials to concrete. The results of GPMs bond strength are compared to OPC mortar as shown in Fig. 19. The bond strength of GPM that was prepared with 5 mass% of MK, 1.16 of $\text{SiO}_2 : \text{Na}_2\text{O}$ and 8% of Na_2O :dry binder displayed highest bond strength of 9.9 MPa and 22.4 MPa in the early (1 day) and late age (28 days), respectively when compared to OPC. Fig. 20 illustrates the typical bond failure of a slant shear sample, where the bonding surface was found to be still intact. The cracks were passed through the NC substrate and GPM interface. Moreover, there was no significant gap between the two bonding surfaces as confirmed by other report [23].

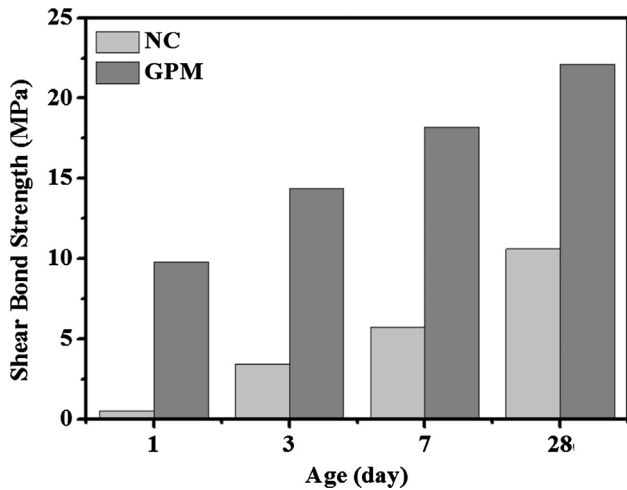


Figure 19. Shear bond strength between OPC (NC) and GPMs with interface line at 45° to the vertical.

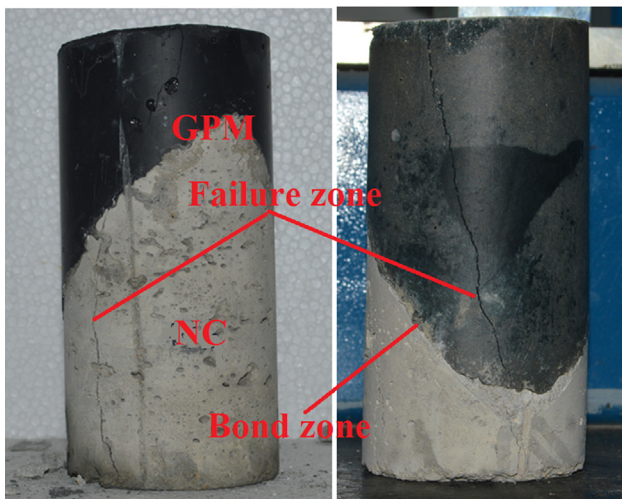


Figure 20. Typical failure modes of GPMs.

4. Conclusion

The impact of MK substituted GBFS on the early mechanical properties of GPMs was determined to examine its feasibility for repair applications. GPM samples were activated with varying solution content (Na_2O :dry binder, and H_2O :dry binder) and alkaline solution modulus (SiO_2 : Na_2O). Performance evaluation of GPMs was conducted at ambient temperature. Based on the achieved results the following conclusions are drawn:

- MK replaced GBFS developed the workability of GPMs, where the setting time was increased and the density was reduced with increasing calcium and silicate contents.
- A reduction in the value of Na_2O :dry binder from 13 to 8% has allowed to develop the early compressive strength as much as 47.84 MPa/24 h as the water content is reduced from 39 to 23%.
- Activation with 1.16 of SiO_2 to Na_2O ratio of the alkaline solution achieved the highest early strength after 24 h.
- These achieved GPMs have demonstrated higher compressive, tensile and flexural strength than that of OPC mortar.
- The attainment of high bond strength of such GPMs indicated their ability as an alternative potential repair material.

References

- [1] Green MF, Bisby LA, Beaudoin Y, Labossière P. Effect of freeze-thaw cycles on the bond durability between fibre reinforced polymer plate reinforcement and concrete. *Can J Civ Eng* 2000;27(5):949–59.
- [2] Lee M-G, Wang Y-C, Chiu C-T. A preliminary study of reactive powder concrete as a new repair material. *Constr Build Mater* 2007;21(1):182–9.
- [3] Yang Q, Zhu B, Zhang S, Wu X. Properties and applications of magnesia-phosphate cement mortar for rapid repair of concrete. *Cem Concr Res* 2000;30(11):1807–13.
- [4] Huseien GF, Mirza J, Ariffin NF, Hussin MW. Synthesis and characterization of self-healing mortar with modified strength. *J Teknol* 2015;76(1).
- [5] Al-Zahrani M, Maslehuiddin M, Al-Dulaijan S, Ibrahim M. Mechanical properties and durability characteristics of polymer-and cement-based repair materials. *Cem Concr Compos* 2003;25(4):527–37.
- [6] Mirza J, Durand B, Bhutta AR, Tahir MM. Preferred test methods to select suitable surface repair materials in severe climates. *Constr Build Mater* 2014;50:692–8.
- [7] Aleem M, Arumairaj P. Geopolymer concrete – a review. *Int J Eng Sci Emerging Technol* 2012;1(2):118–22.
- [8] He Y, Cui X-m, Liu X-d, Wang Y-p, Zhang J, Liu K. Preparation of self-supporting NaA zeolite membranes using geopolymers. *J Membr Sci* 2013;447:66–72.
- [9] Wang K-T, He Y, Song X-L, Cui X-M. Effects of the metakaolin-based geopolymer on high-temperature performances of geopolymer/PVC composite materials. *Appl Clay Sci* 2015;114:586–92.
- [10] Zhang J, He Y, Wang Y-P, Mao J, Cui X-M. Synthesis of a self-supporting faujasite zeolite membrane using geopolymer gel for separation of alcohol/water mixture. *Mater Lett* 2014;116:167–70.
- [11] Zhang Z, Wang K, Mo B, Li X, Cui X. Preparation and characterization of a reflective and heat insulative coating based on geopolymers. *Energy Build* 2015;87:220–5.
- [12] Davidovits J. Geopolymer chemistry and applications. Saint-Quentin (FR): Geopolymer Institute; 2008. ISBN 978-2-9514820-1-2.
- [13] Zhang Z, Zhu H, Zhou C, Wang H. Geopolymer from kaolin in China: an overview. *Appl Clay Sci* 2016;119:31–41.
- [14] Duxson P, Provis JL, Lukey GC, Van Deventer JS. The role of inorganic polymer technology in the development of 'green concrete'. *Cem Concr Res* 2007;37(12):1590–7.
- [15] Malhotra VM, Mehta PK. Pozzolanic and cementitious materials. Taylor & Francis; 1996.
- [16] Sabir B, Wild S, Bai J. Metakaolin and calcined clays as pozzolans for concrete: a review. *Cem Concr Compos* 2001;23(6):441–54.
- [17] Van Deventer JS, Provis JL, Duxson P. Technical and commercial progress in the adoption of geopolymer cement. *Miner Eng* 2012;29:89–104.
- [18] Bernal SA, Provis JL, Rose V, De Gutierrez RM. Evolution of binder structure in sodium silicate-activated slag-metakaolin blends. *Cem Concr Compos* 2011;33(1):46–54.
- [19] De Silva P, Sagoe-Crenstil K. The effect of Al_2O_3 and SiO_2 on setting and hardening of Na_2O - Al_2O_3 - SiO_2 - H_2O geopolymer systems. *J Aust Ceram Soc* 2008;44(1):39–46.
- [20] Chindaprasirt P, De Silva P, Sagoe-Crenstil K, Hanjitsuwan S. Effect of SiO_2 and Al_2O_3 on the setting and hardening of high calcium fly ash-based geopolymer systems. *J Mater Sci* 2012;47(12):4876–83.
- [21] Hu S, Wang H, Zhang G, Ding Q. Bonding and abrasion resistance of geopolymeric repair material made with steel slag. *Cem Concr Compos* 2008;30(3):239–44.
- [22] Pacheco-Torgal F, Castro-Gomes J, Jalali S. Adhesion characterization of tungsten mine waste geopolymeric binder. Influence of OPC concrete substrate surface treatment. *Constr Build Mater* 2008;22(3):154–61.
- [23] Phoo-ngernkham T, Maegawa A, Mishima N, Hatanaka S, Chindaprasirt P. Effects of sodium hydroxide and sodium silicate solutions on compressive and shear bond strengths of FA-GBFS geopolymer. *Constr Build Mater* 2015;91:1–8.
- [24] Phoo-ngernkham T, Sata V, Hanjitsuwan S, Ridditirud C, Hatanaka S, Chindaprasirt P. High calcium fly ash geopolymer mortar containing Portland cement for use as repair material. *Constr Build Mater* 2015;98:482–8.
- [25] Huseien GF, Mirza J, Ismail M, Hussin MW. Influence of different curing temperatures and alkali activators on properties of GBFS geopolymer mortars containing fly ash and palm-oil fuel ash. *Constr Build Mater* 2016;125:1229–40.
- [26] Ismail M, Yusuf TO, Noruzman AH, Hassan I. Early strength characteristics of palm oil fuel ash and metakaolin blended geopolymer mortar. *Advanced materials research*. Trans Tech Publ; 2013. p. 1045–8.
- [27] Astm C. 618. Standard specification for fly ash and raw or calcined natural pozzolan for use as a mineral admixture in Portland Cement Concrete; 2003.
- [28] Committee A. C09. ASTM C33–03, Standard Specification for Concrete Aggregates. ASTM International; 2003.
- [29] Standard A. A109, 2012;". Standard Test Method for Compressive Strength of Hydraulic Cement Mortars Using 2-in Cube Specimens," ASTM International, West Conshocken, PA, 2012, DOI 10.1520/A0307-12, www.astm.org.
- [30] Norma A. C496/C496M-11, Standard test method for splitting tensile strength of cylindrical concrete specimens. C.
- [31] ASTM C. Standard Test Method for Flexural Strength of Concrete (Using Simple Beam with Third-Point Loading). Philadelphia, PA: American Society for Testing and Materials; 1999.

- [32] ASTM C. 882-91-Standard test method for bond strength of epoxy resin system used with concrete by slant shear. American Society for Testing Materials, ASTM; 1991.
- [33] Sofi M, Van Deventer J, Mendis P, Lukey G. Engineering properties of inorganic polymer concretes (IPCs). *Cem Concr Res* 2007;37(2):251–7.
- [34] Al-Majidi MH, Lampropoulos A, Cundy A, Meikle S. Development of geopolymer mortar under ambient temperature for in situ applications. *Constr Build Mater* 2016;120:198–211.
- [35] Lee N, Kim E, Lee H. Mechanical properties and setting characteristics of geopolymer mortar using styrene-butadiene (SB) latex. *Constr Build Mater* 2016;113:264–72.
- [36] Kumar S, Kumar R, Mehrotra S. Influence of granulated blast furnace slag on the reaction, structure and properties of fly ash based geopolymer. *J Mater Sci* 2010;45(3):607–15.
- [37] Sugama T, Brothers L, Van de Putte T. Acid-resistant cements for geothermal wells: sodium silicate activated slag/fly ash blends. *Adv Cem Res* 2005;17(2):65–75.
- [38] Rattanasak U, Chindaprasit P. Influence of NaOH solution on the synthesis of fly ash geopolymer. *Miner Eng* 2009;22(12):1073–8.
- [39] Lin KL, Shiu HS, Hwang CL, Cheng A, Cheng TW. Effects of SiO₂/Na₂O molar ratio on properties of TFT-LCD waste glass-metakaolin-based geopolymers. *Environ Progr Sustain Energy* 2014;33(1):205–12.
- [40] Dombrowski K, Buchwald A, Weil M. The influence of calcium content on the structure and thermal performance of fly ash based geopolymers. *J Mater Sci* 2007;42(9):3033–43.
- [41] Zuhua Z, Xiao Y, Huajun Z, Yue C. Role of water in the synthesis of calcined kaolin-based geopolymer. *Appl Clay Sci* 2009;43(2):218–23.
- [42] Lee W, Van Deventer J. The effects of inorganic salt contamination on the strength and durability of geopolymers. *Colloids Surf, A* 2002;211(2):115–26.



Mohammad Ismail Professor in Department of Structure and Materials, Faculty of Civil Engineering, Universiti Teknologi Malaysia.



Sib.K. Ghoshal Professor in Department of Physics, AOMRG, Faculty of Science, Universiti Teknologi Malaysia.



Ghasan Fahim Huseien PhD student in Department of Structure and Materials, Faculty of Civil Engineering, Universiti Teknologi Malaysia.



Dr. Mohd Azreen bin Mohd Ariffin Senior Lecturer in Department of Structure and Materials, Faculty of Civil Engineering, Universiti Teknologi Malaysia.



Jahangir Mirza Professor in Department of Materials Science, Research Institute of Hydro-Quebec, Quebec, Canada.